Carbon Content Detection in High Temperature and High Pressure Fields Using Laser Induced Breakdown Spectroscopy

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Summary

1. INTRODUCTION

It has become increasingly important to monitor plant condition factors in order to improve the operation of industrial plants, and improved on-line monitoring techniques for plant controlling factors are necessary to enhance the controllability of overall plant operations. Carbon content is an important factor in the operation of pulverized coal thermal power plants, and associated monitoring and control techniques are needed for continued operational improvement. Carbon content is also a key factor for the recycling of fly ash.

Because of their high sensitivity, laser techniques make it possible to monitor these parameters. Strong signal intensity and simple apparatus make laser induced breakdown spectroscopy (LIBS) suitable for composition measurement in gas, liquid, and solid materials (1)(2)(3). LIBS has also been utilized in high pressure and high temperature applications (4). In this study a LIBS technique was applied to detect carbon content in pulverized coal, char, and fly ash under the high pressure and high temperature conditions that characterize IGCC thermal power plants. The results obtained by means of the LIBS technique were compared to those from conventional methods, and the applicability of LIBS to actual plant conditions is discussed.

2. LIBS

In the LIBS process, a laser beam is focused onto a small area, producing hot plasma. The temperature of the plasma can reach 10,000K to 20,000K and the material inside the measurement area is quickly atomized. The atomized material produces an emission dependent upon the material content. The resulting signal is a function of material components, and concentration can be detected by means of analysis.

3. EXPERIMENTAL APPARATUS

The experimental apparatus consists of a high pressure and high temperature furnace and a LIBS unit. The furnace used can produce various conditions in the 300K - 10000K temperature and 0.1MPa - 3MPa (100-3000 Atm) pressure ranges. Pulverized coal, char, and fly ash were added to high temperature and pressure gases using a feeder, and carbon content detectability was tested with various gas compositions and particle densities appearing in actual plants. A LIBS analyzerwas connected to this furnace using a high pressure duct.

A fully automated LIBS system was developed and applied in this experiment to demonstrate actual power plant monitoring. As the actual application was being considered, signal detection was fully automated and the results could be transferred to other computers. Two windows were employed in case of high pressure gas leakage. If a pressure increase is detected at the pressure sensor between the two windows, the valve is closed automatically and measurement is stopped by the system computer.

4. RESULTS

The main species of the fly ash, i.e., Si, Al, Fe, Ca, and C, can be detected in the wavelength range of 240mm - 340nm. These signals were used for the species concentration and plasma status correction. In the case of high pressure conditions, several difficulties are associated with the detection of the C signal. In particular, the ratio of C and Si is characterized by pressure dependence. Si is a major species in fly ash and this ratio allows a rough estimate of the carbon content. This ratio rapidly decreases as the pressure increases, which means that the C signal becomes difficult to detect, while the pressure can also affect the delay time of the C signal intensity. The S/N ratio also depends on the pressure and the delay time. As the pressure increases, the C signal tends to appear with a shorter delay time, and it tends to disappear rapidly. The collision effect is enhanced at high pressure, and the plasma temperature decreases rapidly. The detection species has its own upper energy levels. As the upper energy level becomes higher, the atoms in this energy level are quenched at a high rate under high pressure. As C has the highest energy level among the species in fly ash, C becomes the most difficult to detect. These phenomena are species-dependent, with these parameters having been determined from the experiment to be input parameters for the automated LIBS system.

The gas composition also affects the LIBS spectra. Under actual exhaust gas conditions, there are molecules that contain C atoms. Breakdown of these gases causes a serious problem in the detection of carbon content in fly ash. In case of N_2 buffer gas, the laser energy affects only the plasma temperature, and this can be calibrated by means of plasma temperature correction. In the case of buffer gas containing CO_2 molecules, a high C signal appears which can be attributed to CO_2 molecule breakdown. This effect is highly dependent on laser power, and appropriate setting minimizes this noise in the C signal. The effect is also dependent on the particle density, temperature, and gas compositions, and the measurement parameters must be determined according to the actual measurement conditions. Unburned carbon in fly ash was measured under conditions of T=570K, and P=0.1MPa, with a buffer gas composition of N_2:74%, H_2O:8%, CO_2:15%, O_2:3%. This is a typical exhaust gas condition for a pulverized coal power plant. Ashes from four different coals were examined and the results show good agreement with conventional methods (i.e., JIS-8815). The carbon content in fly ash could be detected even in the presence of CO_2 molecules. A low CO_2 condition usually tends to give better results and to be less affected by the measurement conditions.

5. CONCLUSIONS

LIBS was applied to carbon content measurement in pulverized coal, char, and fly ash, and its applicability was tested under several gas conditions. Improved characteristics were demonstrated in terms of on-line capability and sensitivity compared to the conventional sampling method. LIBS features detection time capability of under 1 minute, as compared to over 30 minutes of sampling and analysis time required by the conventional method. LIBS therefore offers important merits as a tool for actual plant monitoring.

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REFERENCES

(1) W.P.Chisholm, DOE-METC-87-6077, (1987), p.119.
(2) D.K.Otteen, et al., Energy & Fuels, Vol.5, No.2,(1991), p.304.
(3) L.W. Peng, et. al., Process Control Qual., Vol.7, No.1,(1995), p.39
(4) Y. Deguchi, et al., IMEKO2000, Proceedings Volume II, (2000), p.179